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INORGANIC DIELECTRICS RESEARCH

PROGRESS REPORT NO. V

Contract No. DA-36-039-sc-89141

November 1, 1962 to February 1, 1963

Signal Corps Research Program  
File No. 01007-PM-62-93-93

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## Part I

### DEVITRIFICATION OF BaTiO<sub>3</sub>

#### Abstract

Time-temperature firings as determined from the crystallization behavior of the barium titanate glass were made as a possible method of controlling crystal size. The dielectric constants and bulk densities of the devitrified composition was increased but the Curie temperature remained in the vicinity of 150°C and the crystal size remained unchanged. Dielectric constant versus temperature measurements of the glass were made and are discussed. Thermal expansions of the glass and crystalline phases of the devitrified bodies were determined. A careful X-ray examination reveals that the only crystalline phase present in the devitrified composition is tetragonal barium titanate, which appears more tetragonal than conventional barium titanate.

Part II

TRANSPARENT POLYCRYSTALLINE CERAMICS

Abstract

Program of sintering alumina compositions in controlled atmospheres is continuing. An investigation has been initiated to study cubic crystalline phases.  $\text{MgAl}_2\text{O}_4$  or "spinel" has been selected for the initial study with substitutions contemplated in the di-valent and tri-valent sites. Compound formation and sintering properties are presently being studied.

Part III

LOW LOSS MICROWAVE DIELECTRICS

Abstract

Most of the difficulties encountered in firing the lanthanum alumino-silicate composition have been alleviated with the use of a pre-fire and a after-fire heat treatment. This technique is presented along with electrical data obtained thus far.

Compositions located within the library of  $\text{MgO-ZrO}_2\text{-TiO}_2$  exhibit low loss electrical properties at 1 and 100 Mc/sec. Several compositions have been prepared and evaluated at 8.5 KMc. The procedures and results are presented.

Part IV

HOT EXTRUSION

Abstract

The successful extrusion of lead zirconate titanate in steel coextrusion cans is described. Attempts to hot extrude barium titanate slowly at low pressure are also described. These experiments give some insight into the flow properties of barium titanate at elevated temperatures.

Progress Report - Part I  
DEVITRIFICATION OF BaTiO<sub>3</sub>

Introduction

When prepared conventionally, ferroelectric barium titanate has a dielectric constant of 1200 in the range from 0°C to 110°C. At the Curie temperature of 120°C the dielectric constant rises abruptly to 6000-8000, then decreases to some low value, the compound no longer being ferroelectric. An inversion from the tetragonal to the cubic phase takes place at this temperature.

Reference has been made in previous reports to Anliker, Brugger, and Kanzig, who examined small, loose particles of barium titanate by X-ray diffraction, electron diffraction, and electron microscopy. They state that the transition from a tetragonal to the cubic phase becomes smeared out over a temperature range which increases with decreasing particle size.

If small crystals of barium titanate could be obtained in the bulk of a ceramic body, the Curie temperature should increase. This is difficult to attain even with small crystals as the starting material since the crystals tend to grow rapidly during firing.

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The making of a barium titanate glass without the use of additives by the flame spray technique, and the subsequent devitrification of this glass into a dense crystalline ceramic body has been discussed in previous reports. This results in the formation of extremely small crystals and an increased Curie temperature of 150°C.

During this report period the following problems have been investigated:

1. Time temperature firings, as determined from the crystallization behavior (DTA and X-ray) of the glass, were made in order to attempt to control crystal size. The resultant crystal size and electrical properties have been evaluated.
2. The electrical properties of the barium titanate glass was determined.
3. The thermal expansion behavior of the barium titanate glass and devitrified barium titanate body were determined.
4. The devitrified body was examined closely for the presence of meta-titanate phases.



### Time-Temperature Firings

#### Procedure

Temperatures were selected from the DTA curve of the ground glass spheres. During the firing cycle specimens were held at these temperatures for a period of three hours. After the three hour soak was completed the bodies were fired to maturity.

The specimens were prepared in the following manner. The flame-sprayed glass spheres (-325) were ground for 2-1/2 hours. A small amount of water was added to the ground spheres and they were then pressed into discs 1/2" in diameter by 0.06" thick. The specimens were fabricated in a hand-operated hydraulic press at 10,000 lbs. pressure. These were fired in a platinum-wound tube furnace with the firing cycle being closely controlled.

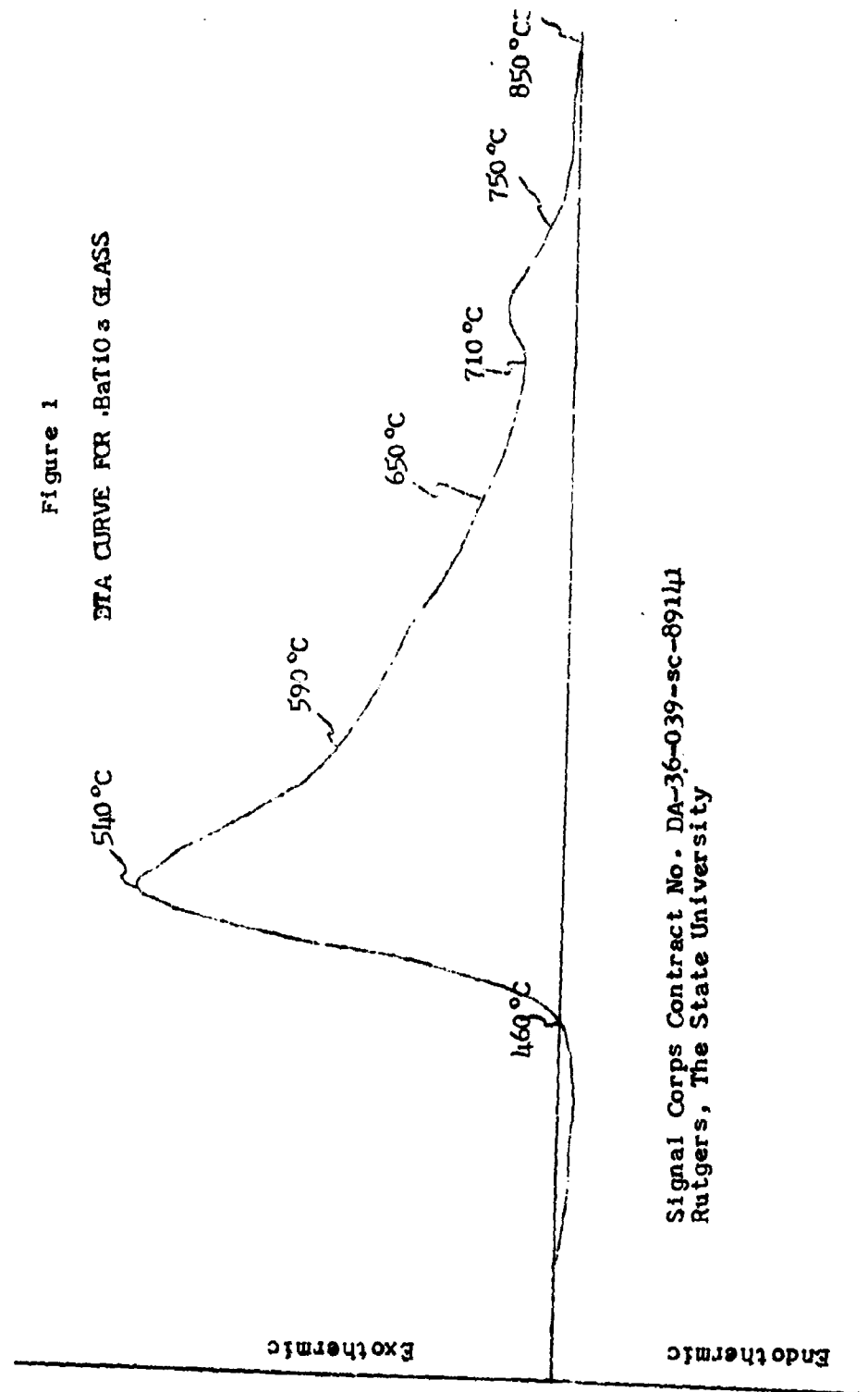
The procedure for preparing samples for electrical testing is as follows: The flat surfaces of each disc were coated with #4351 silver preparation manufactured by the DuPont Company and allowed to dry in an oven at 70°C. A bath of Dow Corning 200 fluid containing a stirring rod and heating element was used to heat the specimens while taking electrical data. The electrical properties, i.e., dielectric constant and power factor, were evaluated at 1Kc per second on a General Radio Impedance Bridge, Type 615 A.

The microstructure was studied using the polished section technique. On a brass lap wheel with silicon carbide paper and water the specimens are ground with grain numbers: 240, 340, and 600. They are then ground in sequence with emery papers (0, 2/ $\sqrt{}$  3/0 and 4/0) and kerosene and polished with fine diamond powder and oil. The mounted specimens were etched with a solution of 1% HNO<sub>3</sub> and 0.5% HF. Crystal size distributions were made and photomicrographs taken.

#### Results and Discussions

The DTA curve for the ground glass spheres is given in Figure 1. There is no observable difference between this and the DTA curve for the unground glass spheres. X-ray diffraction patterns of draw trial samples substantiate the DTA observations. A crystalline peak appears at 450°C, which broadens considerably at 650°C.

Specimens were held at 450°C, 650°C, 750°C, and 850°C for three hours each and then fired to 1320°C which is the maturing temperature. The bulk densities and electrical data are summarized in Table 1 and plotted in Figures 2 and 3.



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TABLE I  
Summary of Results

<u>Firing Schedule</u>	<u>Bulk Density (g/cc)</u>	<u>Dielectric Room Temperature</u>	<u>Curie Temperature Constant</u>
1320 °C	5.54	1340	2400
450 °C + 3 hours; 1320 °C	5.55	1370	2420
650 °C + 3 hours; 1320 °C	5.60	1580	2840
750 °C + 3 hours; 1320 °C	5.53	1320	2380
850 °C + 3 hours; 1320 °C	5.52	1300	2370

The Curie temperature remained between 145-150 °C, no increase or decrease being noted. The 650 °C soak produced an increase in the amount of crystallization bulk density and dielectric constant. The room temperature and Curie temperature dielectric constants were 1580 and 2840 respectively as compared to the 1340 and 2400 values of the body fired directly to maturity with no additional firing treatment. The bulk density was increased from 5.54 to 5.60 g/cc. Incremental improvement was attained with the

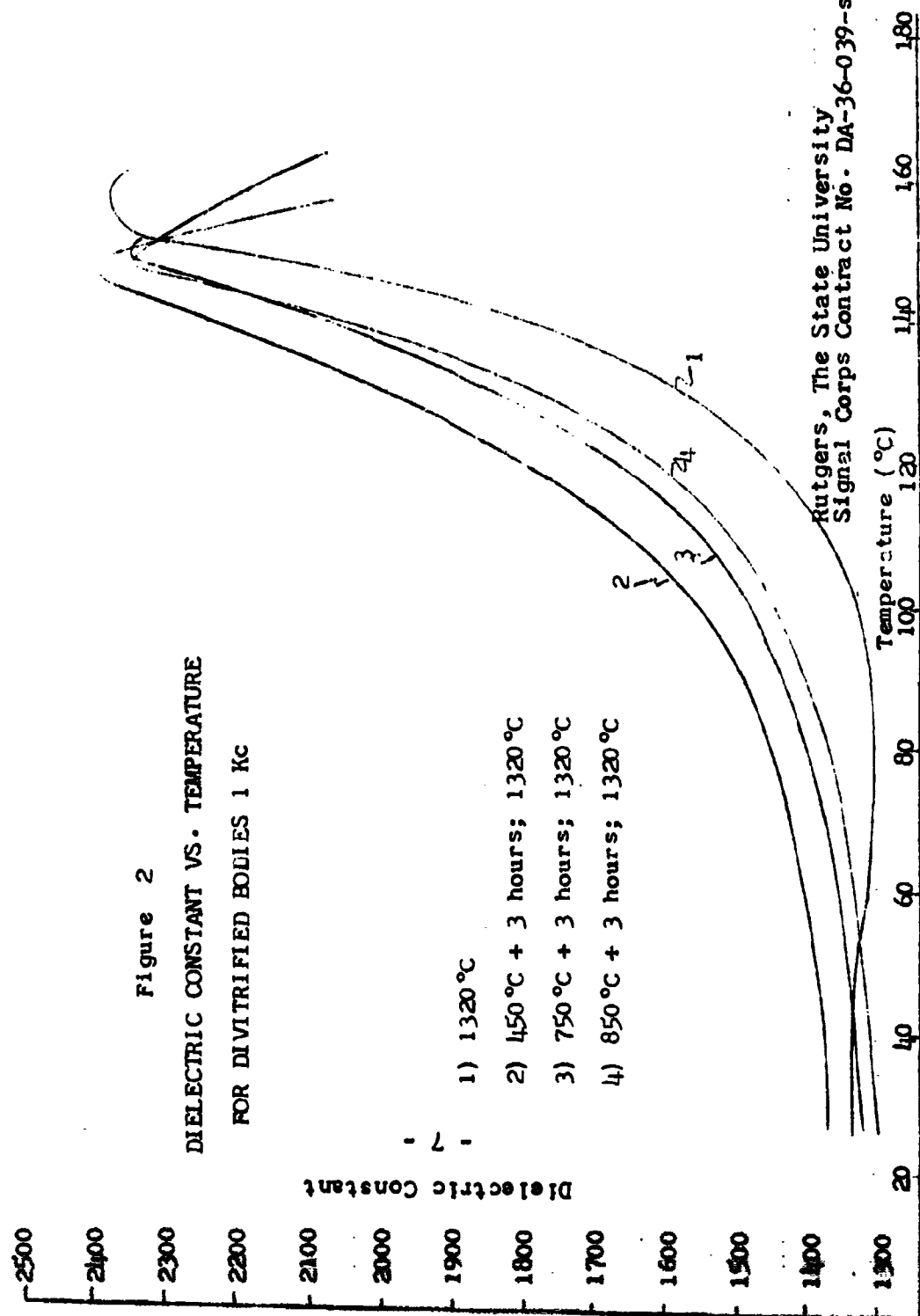
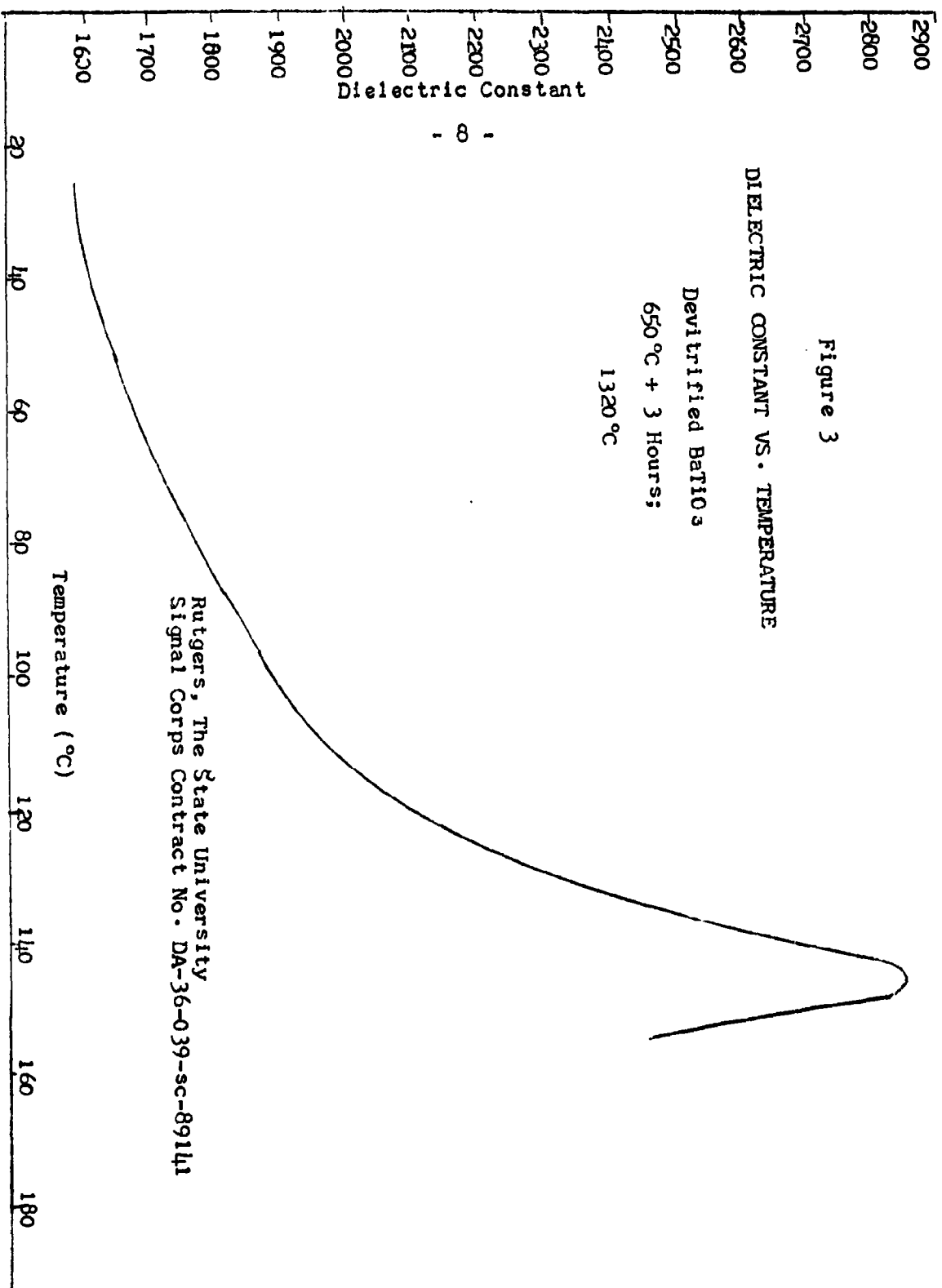


Figure 2  
 DIELECTRIC CONSTANT VS. TEMPERATURE  
 FOR DIVITRIFIED BODIES 1 Kc

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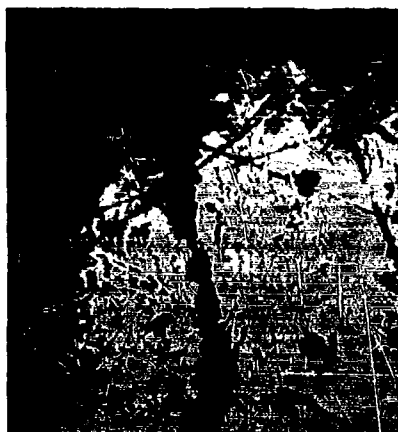




650 °C + 3 hours;  
1320 °C

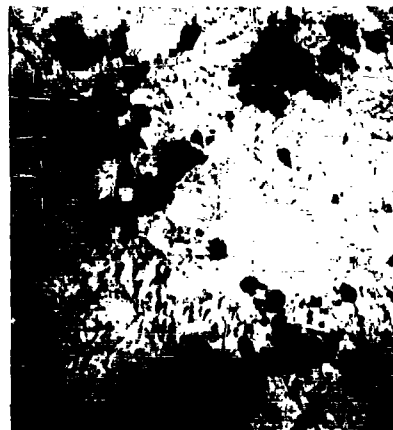


450 °C + 3 hours;  
1320 °C

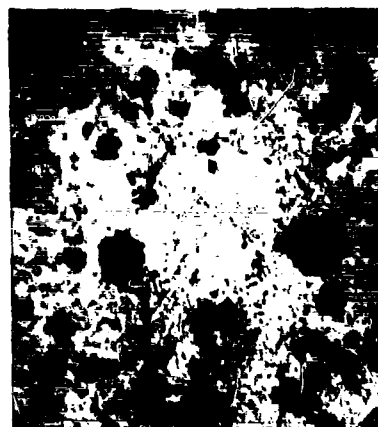


1320 °C

Figure 4  
Photomicrographs of Devitrified  
BaTiO<sub>3</sub>



850 °C + 3 hours;  
1320 °C



750 °C + 3 hours;  
1320 °C

Magnification 320X

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firing at 450°C. The temperature coefficients of the bodies which were given the time-temperature treatment are highly positive.

No change occurred in crystal size in the fired ceramic during the soak treatment, the size distribution remaining between the limits of microscopic resolution and 4 microns as in the devitrified composition fired directly to 1320°C. The microstructures can be observed in the photo-micrographs in Figure 4 taken at 320X. The dendritic effect which was observed at 1320°C in the low bulk density devitrified bodies reported previously is also present in the densified bodies. By 1355°C the dendritic-like appearance has changed to one that is characteristic of normal barium titanate crystals as also noted in the low density bodies. It is interesting to note that though the crystalline content has been increased somewhat the crystal size distribution remains unchanged for all fires including no soak. The crystal size distribution is between the limit of resolution of the microscope (approximately 0.2 $\mu$ ) and 4 $\mu$ .

#### Investigation of Barium Titanate Glass - Electrical Properties

##### Procedure

In order to determine the dielectric constant, some of the ground glass spheres were compacted into a disc under



considerable pressure to a porosity of 30%. The measured dielectric constant was then corrected for porosity. The specimens were silvered. Cross-sections of the pieces observed under a binocular microscope showed that silver remained on the surface and did not flow into the sample. The samples were immersed in a silicone oil bath for dielectric constant versus temperature measurements and because of their heavy compaction remained intact.

#### Results

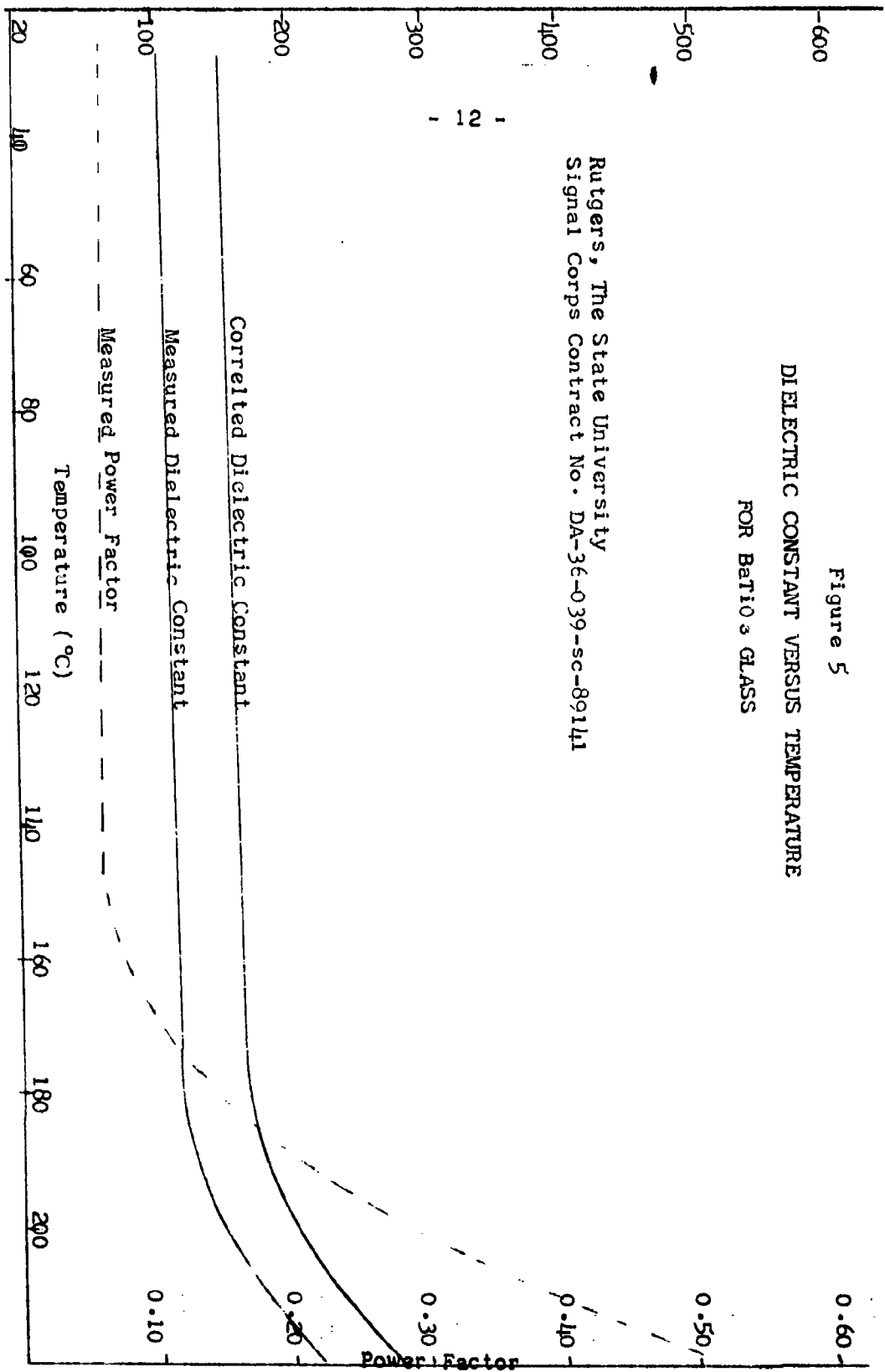
The measured and porosity - corrected dielectric constants are plotted against temperature in Figure 5. The corrected dielectric constant of the glass is at 150. This remains constant until about 180°C at 1Kc at which time it increases rapidly as would be expected. This is associated with the increase in measured power factor which begins to rise at 160°C. This corresponds to the rise in power factor in the devitrified body, which may very well arise from the electrical behavior of the glass matrix. The existence of ferroelectricity in the glass was not detected and this consideration is therefore eliminated as a possible mechanism.

#### X-Ray Investigation

An indexing of Debye-Scherer film strips by the

Figure 5  
 DIELECTRIC CONSTANT VERSUS TEMPERATURE  
 FOR BaTiO<sub>3</sub> GLASS

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Straumanis technique shows that the only crystalline phase present in the devitrified bodies is tetragonal barium titanate. There are no meta-titanates, titania or other crystalline phases.

#### Thermal Expansion Characteristics

It is important to determine whether the system is under stress. As observed from the microscopic studies, the microstructure consists of single crystals embedded in a matrix material which is considered to be a barium titanate glass. It is important then to have some idea of the state of stress that may be induced in the crystal by the glass during the cooling cycle of the devitrification firing since this may contribute to the Curie region phenomena hitherto discussed. This has been approached from an investigation of the thermal expansions of the glass, crystal, and glass-crystal composite.

The crystal and devitrified body total linear thermal expansions were measured by interferometric means. The glass was ground and compacted under considerable pressure into bars 2 inches in length and .05 inches in diameter with a porosity of about 25%. The thermal expansion were measured on a dilatometer. The results appear to be reliable for at least the first 150°C.

The results are shown in Figures 6 and 7. In Figure 6 is shown a plot of the total linear thermal expansions of the solid sintered crystalline bodies and the devitrified specimens. The expansion of the crystalline material is characteristic of barium titanate showing a discontinuity in the Curie region. The glass-crystal composite behaves similarly above and below the Curie temperature but in the range 100°C-180°C does not show the sharp discontinuity of the crystalline sample. It is leveled out, but still is continuous. This may very well be associated with the mechanism that is responsible for the structural and dielectric phenomena observed in this region. Further the devitrified body exhibits a lower expansion curve than the crystalline bodies.

The expansions are enlarged in Figure 7 and are shown with that of the glass for the sake of comparison. Up to the conventional Curie region, the expansion of the glass is less than that of the crystalline and this is reflected in the expansion of the glass-crystal composite above the expansion of the glass is greater. When the devitrified bodies are cooled from 1320°C during the devitrification and densification firing, this difference in thermal expansions between the glass and crystalline phases may be associated with the mechanisms contributing to the other observed behaviors.

Figure 6

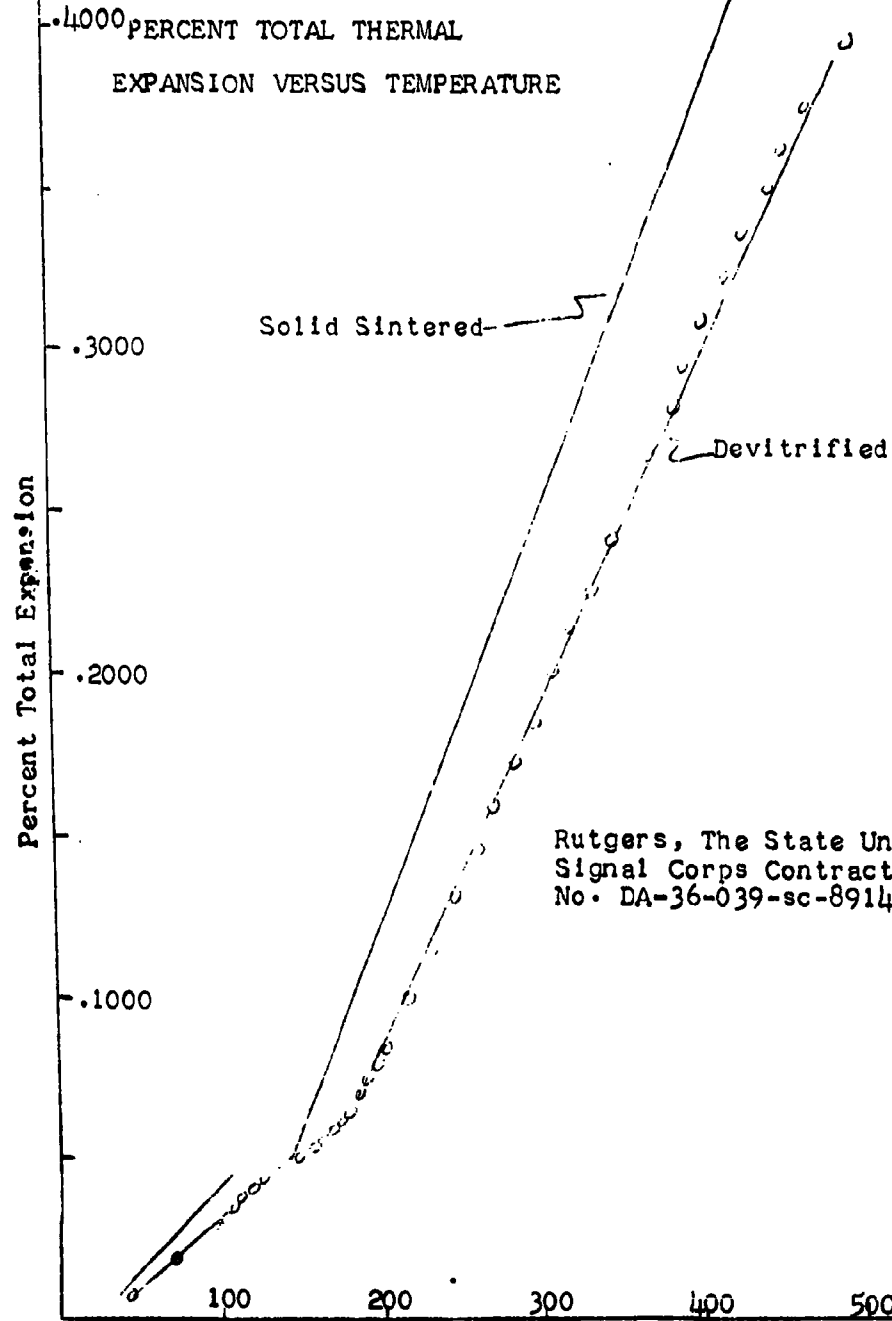
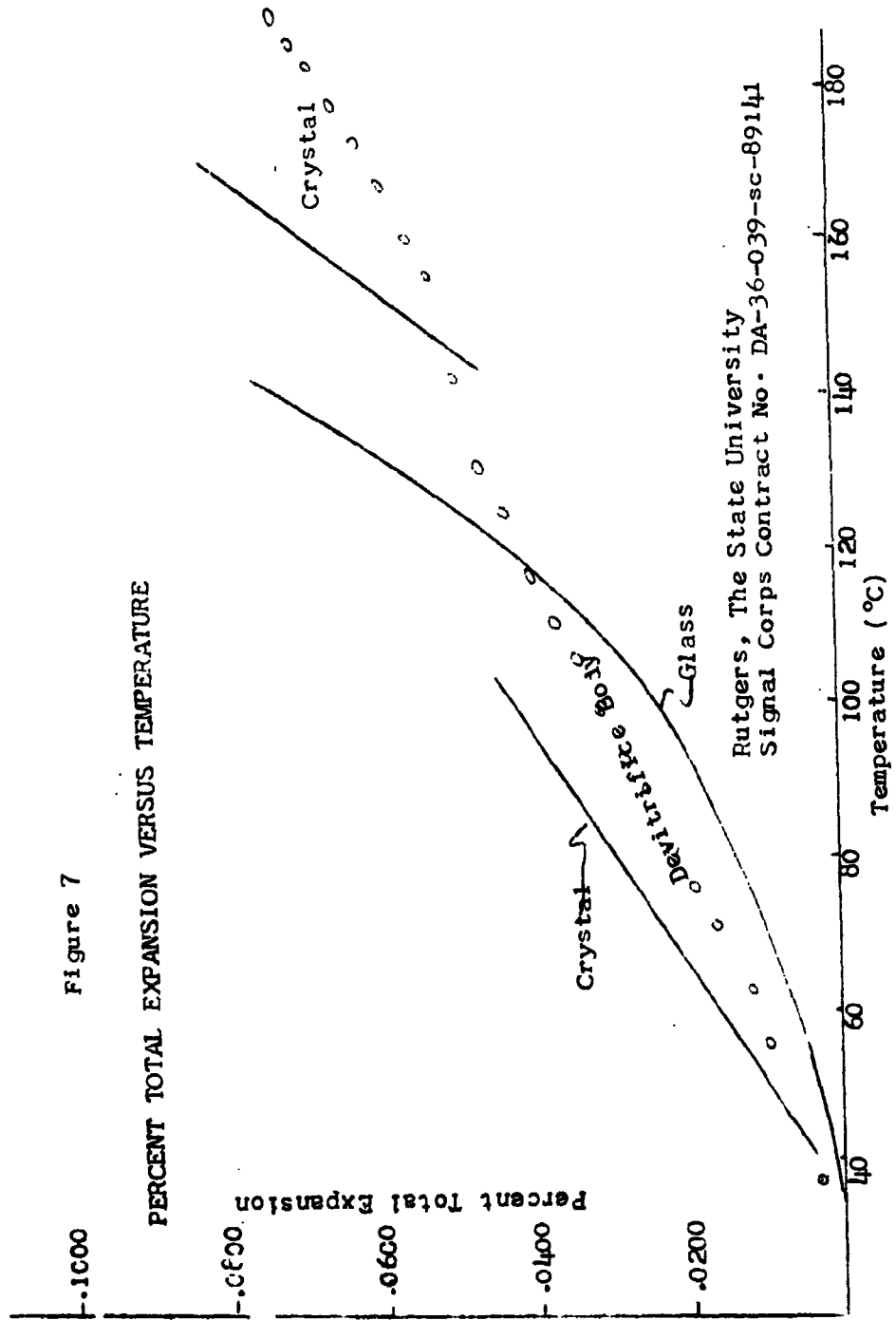


Figure 7

PERCENT TOTAL EXPANSION VERSUS TEMPERATURE



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The precise room temperature lattice constants of the tetragonal barium titanate in the devitrified body have been determined from the Bragg angles in the back-reflection region of the Debye-Scherrer film by the method of least squares. The following values were calculated:

$$\begin{aligned}a &= 3.988 \quad \pm 0.004 \\c &= 4.043 \quad \pm 0.004 \\c/a &= 1.013\end{aligned}$$

The ASTM X-ray cards with a National Bureau of Standards reference gives the following for barium titanate.

$$\begin{aligned}a &= 3.994 \\c &= 4.038 \\c/a &= 1.010\end{aligned}$$

A comparison of this data indicates that there maybe an increase in the tetragonality of the barium titanate formed in the divitrified material.

Most of these reported results have been realized very recently and time has not permitted thorough analysis of their significance and contribution to the unusual effects attained in this study. This will be done and reported in the next report.

Note: It has recently been discovered that the stoichiometry is off in the flame-sprayed barium titanate glass, and that this is due to the solutions of BaO from the glass spheres on entering the quenching medium namely water. This is being double checked and methods are being evaluated to prevent the BaO solute. Attempts are being made to start with an excess of BaO and this is being evaluated.

#### Summary

Time-temperature firings of specimens prepared from ground barium titanate glass with soaking periods as determined from the crystallization behavior (DTA and X-ray) were made. Although the per cent of crystalline phase present and the dielectric constants were increased, the Curie temperature remained in the vicinity of 150°C. Crystal size was not changed by this treatment, remaining between the limits of microscopic resolution and  $4\mu$ . The barium titanate glass was shown to be a high dielectric constant material, the value being about 150 when corrected for the porosity factor. This remains constant until about 100°C at 1Kc at which point it increases rapidly, the measured power factor also increasing. The thermal expansion of the glass was shown to be less than that of crystalline barium titanate up to the conventional Curie region and is greater above it. The thermal expansion of the devitrified body levels out in the Curie region but does not show the discontinuity of the solid sintered.



No meta-titanate crystalline phases are present, only tetragonal barium titanate. Further the tetragonality of the devitrified barium titanate has been increased as compared to the normal crystalline phase.

#### Future Work

1. Study the findings presented above and assess their contributions to the unusual properties of the system under study.
2. Determine the significance of the stoichiometry of the system under study.
3. Determine procedures prevent solubility of BaO from glass during flame spraying.
4. Determine exact mechanism of increased Curie temperature in the system under study.

Progress Report - Part II

TRANSPARENT POLYCRYSTALLINE CERAMICS

Introduction

The objective of this phase of the program is the development of a translucent to transparent polycrystalline ceramic body having an extremely smooth surface, comparable to plate glass, to permit its use as a substrate for the deposition of a uniform ultra-thin metallic film with good adherence. Possible ultimate uses for this material is in ultrasonic delay lines, in infrared devices, and as tube envelopes. The body may be of a pure oxide or compounds.

For optimum engineering properties, as well as the development of transparency, the material must have an extremely high per cent of true density. The presence of voids in a finished piece is one of the most detrimental properties, as they affect other properties in a detrimental manner. Their presence in a body causes variation in strength, electrical properties, machinability, and various other properties.

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The degree of transparency is determined by the amount of in-line transmissivity of radiant energy of varying wavelengths through the body. Pores, which are caused by gases trapped within the body, scatter light rays and in effect increase the path length through a solid. Grain boundary cracks resulting from abnormal or excessively large rates of grain growth act essentially as pores in their effect on transmissivity; that is, boundary cracks increase the path length and reduce the resultant transparency of the body. Grain growth must be sufficiently suppressed to avoid grain boundary cracking and also to prevent trapping of pores within the body.

#### Sintering of Alumina

The results to date of this phase of the investigation were reported in the previous progress report, dated November 1, 1962. On page 33 of that report can be found a diagram of the furnace being used in this investigation. It is possible to fire this furnace at temperatures up to 1900°C in various atmospheres. Hydrogen, argon, and oxygen have been utilized to date, with the possibility of vacuum being used in the future.

The body is made by firing compacts of extremely pure and extremely fine alumina powder. The alumina used is Linde "A", 99.9+%  $\text{Al}_2\text{O}_3$ , and 0.3 $\mu$  and finer in size. The problem of excessive grain boundary cracking, excessive rate of grain growth, and consequent pore entrapment is overcome by the addition of 0.25% by weight of magnesia and by an initial or first firing stage which causes grain growth to proceed at a relatively slow rate and permit trapped gas to escape from the body. The first firing is at 1700°C while the second is at 1900°C. Even though the rate of grain growth is somewhat higher at the elevated temperatures, it takes place only for a limited period.

The highest densities attained so far have been with the specimens fired in oxygen. A bulk density of 3.93, or 98.5% of theoretical single crystal density was achieved. However, no appreciable degree of transparency was obtained.

There has been considerable delay involved in this phase of the investigation, due to troubles with the furnace. Originally, it was designed to be used with an existing coil. However, due to a very short hot zone, and the coil being too large in diameter, it was impossible to attain the desired temperature. The problem was referred to the manufacturer, who designed a new coil.

When the coil arrived and was hooked up to the furnace, it was found that the desired temperature still could not be reached. Due to improper coupling, the voltage and amperage were out of phase and full power could not be drawn from the generator. It was determined that the problem was due to insufficient capacitance in the generator. Therefore, another capacitor was purchased and connected to the generator circuit.

With the new coil and the additional capacitor the furnace worked efficiently and several firings were made at 1900°C. However, an unfortunate accident recently occurred and the outer, or gas-containing tube cracked. The furnace is now inoperative until a new tube is obtained. In the meantime, work is being planned on other phases. As has been mentioned previously, cubic crystalline phases must eventually be utilized to eliminate anisotropy and obtain optimum results.

#### Investigation of Cubic Phases

A possible material for study is  $MgAl_2O_4$ , which is identified as "spinel". The properties of this material, as compared with those of the single oxides are as follows:

<u>Material</u>	<u>Formula</u>	<u>Density</u>	<u>Melting Point</u>
Alumina	$Al_2O_3$	3.987	2050°C
Magnesia	MgO	3.65	2800°C
Spinel	$MgAl_2O_4$	3.6	2135°C

Sapphire can be converted into spinel by means of the vapor phase. In an atmosphere of hydrogen, the reaction proceeds inwardly from all the outer surfaces, and with time the entire sapphire sample may be converted to spinel. In an oxidizing atmosphere, spinel is formed only at the area of contact between  $MgO$  and  $Al_2O_3$ .

Naviask prepared spinel by placing small sapphire samples directly on blocks of periclase. Firings were done in atmospheres of hydrogen, argon, and air; and in vacuum. Temperatures ranged from 1500 to 1900°C. In a hydrogen atmosphere at 1900°C, a spinel layer 48 mils thick was obtained in 16 hours. At 1800°C a 21 mils thick layer was obtained in 6.4 hours. Results with vacuum were comparable to those obtained with hydrogen.

Spinel is usually prepared in large quantities by heating the oxide powders together. Low loss ceramic dielectric with spinel as the principal phase has been prepared at Rutgers.<sup>a</sup> An addition of 10 to 20% silica, to the magnesia - alumina mixture resulting in spinel, yields strong dense bodies of L-6 grade. When the batch formula consists of magnesia, alumina, and clay, the bodies mature between

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<sup>a</sup> Louis Navias, "Preparation and Properties of Spinel Made by Vapor Transport and Diffusion in the System  $MgO \cdot Al_2O_3$ ," J.A.C.S. 44:9, p. 434 (1961)

<sup>a</sup> Edward J. Smoke, "Spinel as Dielectric Insulation," Ceramic Age, May 1954.

2650 and 2800 °C; the only crystalline phase identified by X-ray analysis is spinel. Spinel can also be formed by adding boric acid or NaCl to the mixture; these additives increase the reaction rate, but the reaction will go to completion with the reagent oxides alone.

In addition to  $MgAl_2O_4$ , there are a number of other oxides of the general formula  $AB_2O_4$ , having a cubic structure. The A constituent may be any one of the following divalent ions: Mg, Fe, Cd, Cu, Mn, Ni, Zn; while the B member may consist of any of the following trivalent ions: Al, Fe, Cr, Ga, In, V. These materials are discussed more fully in the following section.

#### Structure of Spinel

In the spinel structure, the oxygen ions are in face-centered cubic close packing. An elementary cell has four atoms, four octahedral interstices, and eight tetrahedral interstices. This makes a total of twelve interstices to be filled by three cations, one divalent and two trivalent. In each elementary cell, there are two octahedral and one tetrahedral site filled. Eight of these elementary cells are arranged so as to form a unit cell containing 32 oxygen ions, 16 octahedral cations, and 8 tetrahedral cations.

Two types of spinel occur. In the normal spinel the  $A^{2+}$  ions are tetrahedral sites and the  $B^{3+}$  ions are on octahedral sites. This is the structure observed for  $ZnFe_2O_4$ ,  $CdFe_2O_4$ ,  $MgAl_2O_4$ ,  $FeAl_2O_4$ ,  $CoAl_2O_4$ ,  $NiAl_2O_4$ ,  $MnAl_2O_4$ , and  $ZnAl_2O_4$ . In the inverse spinels, the  $A^{2+}$  ions and half of the  $B^{3+}$  ions are on octahedral sites, whereas the other half of the  $B^{3+}$  are on tetrahedral sites. This is the more common structure and is observed for  $MgFe_2O_4$ ,  $Fe_3O_4$ , and many other of the ferrites.

One of the most important properties of spinels is the ease with which they can enter into partial substitution with each other. In fact, all naturally occurring spinels are mixtures, and the pure spinels can only be prepared artificially. However, it is not known whether unlimited solid solution can take place with any spinel. All of the aluminates are probably miscible with each other, as are the ferrites and chromites, but it is not known if the aluminates are miscible with the ferrites in all proportions.

#### Program of Study

Magnesium aluminate,  $MgAl_2O_4$ , is the best spinel to study first. The program is already underway. In order to insure through mixing of very fine particles to aid in the



formation of the spinel, the raw materials selected are reagent grade magnesium sulphate and C.P. aluminium ammonium sulphate. These, when mixed in the correct proportions and allowing for the loss of the volatile constituents, actually go through a liquid phase below 1400°F which results in very intimate mixing. Continued heating to 1800°F and above results in a calcined material which exhibits spinel functions. This calcine is then powdered and pressed into specimens and fired.

At the present time the maturing characteristic of this composition is being evaluated with the firings being done in air. Quality and properties will be determined. If the percentage of true density is too low, sintering studies will be initiated in other atmospheres such as oxygen, hydrogen, and vacuum. After the  $MgAl_2O_4$  crystalline phase has been evaluated the substitutional studies will be started.

#### Future Work

1. The work on alumina will be completed.
2. The cubic crystalline phases, in particular spinel ( $MgAl_2O_4$ ), will be studied.

Progress Report - Part III

LOW LOSS MICROWAVE DIELECTRICS

Introduction

The object of this investigation is to develop a dielectric material having a dielectric constant of approximately 15 and a power factor not to exceed .0004 at the microwave frequencies and in the temperature range -50 to 300°F. This dielectric constant is above that for normal insulation.

In previous reports, fabrication techniques were evaluated and some dielectric data was presented for the lanthana alumina silica ternary. In this report the pre firing technique will be fully presented along with electrical data accumulated..

Compositions located within the ternary  $MgO-ZrO_2-TiO_2$  exhibit electrical properties as described above at 1 and 100 Mc/sec. Several compositions have been prepared and evaluated at 8.5KMc. Procedure and results are presented.

Lanthanum Alumino Silicate Dielectrics

Introduction

In previous reports various fabrication techniques were evaluated. In the course of this investigation it was found that only pre-firing gave reliable results. Various containers were used but only alumina containers gave results that were

relatively free from contamination. This technique will be discussed along with electrical properties obtained throughout the ternary system.

#### Experimental Work

The material in disc form was placed on  $\text{La}_2\text{O}_3$  powder which had been previously heated at  $1200^\circ\text{F}$  for 6 hours to insure thorough drying. The powder was placed in the bottom of a closed impervious alumina container. This container was then placed inside of an induction furnace and fired. The composition that was tested in this set-up was LSA-5 (Table III).

The preparation of this composition is similar to that of K15+1. First, the  $\text{La}_2\text{O}_3$  is dried at  $1200^\circ\text{F}$  for 6 hours in glazed crucibles. Upon cooling this oxide to about  $100^\circ\text{F}$ , it is weighed out along with  $\text{Al}_2\text{O}_3$  and  $\text{SiO}_2$ . As soon as it is weighed, the batch, containing about 200 grams of material, is then placed into a quart-sized alumina mill along with approximately ten alumina balls. The reason for the small number of milling balls is that the batch is only to be mixed and is not to be ground to a smaller particle size. Next, toluene is added as the dispersant. The ball mill is then sealed and immediately placed on a mill and mixed for 20 hours. The next day the mills were removed from the mixing

apparatus and their contents were vacuum filtered. The need for vacuum filtering arose from the difference in specific gravity of the oxides used. Since  $\text{La}_2\text{O}_3$  has a high specific gravity, it would have a tendency to settle out of the batch first causing a non-uniform batch composition. After filtering the batch was then placed in enameled pans and left under an evacuating hood for two days in order to dry out the batch. After the batch was then passed thru a 200-mesh screen.

This powder was then pressed dry into discs at 1.250 inches in diameter and about 1 inch in thickness. Usually three of these slugs are pressed. When these slugs are placed on top of each other in the alumina container, it is noted the center part of the middle slug constitutes the "hot zone" in the induction furnace during firing. The furnace is then turned on and taken up to the maturing temperature in about two hours and then soaked for about 15 minutes. The temperature is determined by sighting an optical pyrometer thru an one-half inch diameter hole drilled in the cover of the alumina container. The temperature readings are taken from the top of the third sample which is somewhat cooler than the middle of the second sample. Uniformly fired samples can't be obtained using a slow rate of raise of temperature during firing and a long soak since this would enable the molybdenum oxide in the atmosphere more time to enter the tube and then to contaminate the slugs.

When the slugs were removed from the furnace, there was about a 1/4 of an inch of material on the top of the third sample and the bottom of the first sample that was partially underfired. The underfired part of the slug was ground off by an alumina grinding wheel and then discarded. Consequently, the temperatures that are given for the prefiring operations are slightly lower than the actual firing temperature of the material used. The slugs were then crushed in an iron mortar and pestle and passed thru a 200-mesh screen. To eliminate some of the contamination arising from crushing, a permanent magnet was passed over the powder. This removed some iron specs but conceivably there might be some iron specs and/or iron smears left in the powder since the spectrographic analysis taken on the powder revealed a trace amount of iron. This powder was then placed in a closed container and 5% (weight) of a 5% (weight) of aerosole and water mixture (AOT) was added. This mixture was added to aid in pressing since it is both a lubricant and a binder. This container of powder and lubricant was left overnight so that the AOT mixture would disperse itself to most of the grains of the powder. The next day the powder was passed thru a 30 mesh screen and then pressed into discs with the dimensions of 9/16 inch in diameter and 1/4 inch in thickness.

The pressure applied to the powder was 10,000 pounds per square inch. This high pressure gave discs that were fairly dense having no cracks, chips or laminations. After repeated firings to obtain the optimum density, the surfaces of the discs were then ground off on a loose grain lap wheel using a 120 mesh particle size silicon carbide grit. The reasons for this operation were threefold. First, the faces of the disc had to be fairly parallel and relatively smooth so that reproducible electrical properties could be obtained; second, the ratio of the diameter to thickness of the disc had to be at least 15 to 1 to attain desirable capacitance value. Third, the surfaces of the discs would not be different due to the impurities encountered from the setter and from the atmosphere. After the grinding operation, the bulk densities and the moisture absorptions were obtained. The discs were then cleaned with carbon tetrachloride to remove any impurities on the surface. The electrodes were applied. This consisted of painting DuPont conductive silver No. 4351 on both sides of the disc. To determine whether a good contact has been attained with the silver paint, samples measured by this technique were also tested by application of an indium-gallium coating. This coating gives a very intimate contact. The results indicated very little difference between the two techniques.

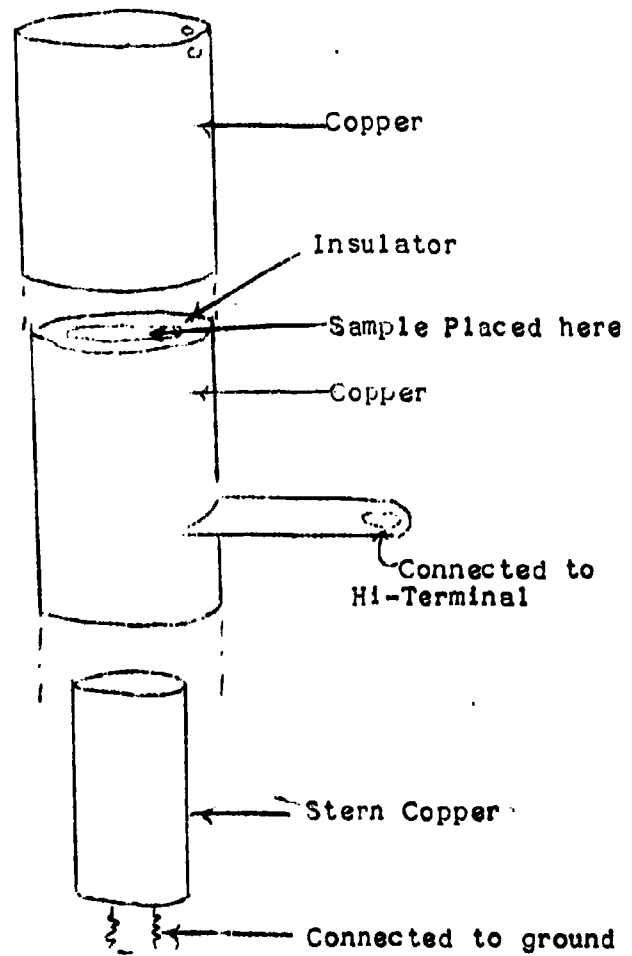
After the electrodes were applied, the samples were tested at 1 megacycle using a Boonton Q-meter, type 260-A. Two different coils were used. One coil was #22 giving a capacitance of 92 and a Q of 200 with a range of 500-1400 KC. The second was a H.-Q coil giving a capacitance of 230 and a Q of 212 X 2.5 at 1 megacycle. Two different methods of making contact to the sample were also employed. The first was a special container shown in Figure 1. The reason for using this apparatus is to decrease the edge effects by containing the stray field within the apparatus. The second method was the General Radio Corporation method of a point contact. All these methods were used to obtain the most reproduceable electrical results.

### Results

Two different firings were made on the LSA-5 composition the temperatures were 2250°F and 2350°F. Both of these compositions were vitrified; however, the composition that was fired to the higher temperature began to slump due to the large amount of glass in the body. The results of this analysis are given in Tables I and II. Along with these results are the preliminary findings using the same composition but utilizing the calcining technique which has already been evaluated.

Figure 1

SAMPLE HOLDER



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Table I

Dielectric Properties of LSA-5

Prefired at 2250°F

In platinum furnace

<u>Sample No.</u>	<u>Discs Temp. (°F)</u>	<u>Atm.</u>	<u>Time (Hr.)</u>	<u>K</u>	<u>Power Factor (1 Mc)</u>	<u>Bulk Density</u>	<u>Moisture Absorp- tion (%)</u>
4	2200	Air	7	12.2	.0019	3.86	.72
5	2240	Air	9	12.4	.0016	3.90	.05
6	2240	Air	3	12.4	.0012	3.94	.07
9	2220	Air	6	12.4	.0013	3.91	.08

In Glo-Bar furnace

3	2120	OX	2	12.0	.0029	3.56	.90
7	2140	Air	2	12.7	.00122	3.97	.09
8	2160*	Air	1-1/2	10.8	.00184	3.74	1.18

\* Recorder started to give faulty readings.

Table II

Dielectric Properties of LSA-5

Prefired at 2350°F

In Platinum furnace

<u>Sample No.</u>	<u>Temp. (°F)</u>	<u>Atm.</u>	<u>Time (Hr.)</u>	<u>K (1Mc)</u>	<u>Power Factor</u>	<u>Bulk Density</u>	<u>Moisture Absorption (%)</u>
12	2220	Air	5	12.1	0.00065	4.01	0.01
12	2180	Air	5	11.5	0.00085	3.96	0.06

In Glö-Bar Furnace

10	2140	OX	1-3/4	11.4	0.00085	3.82	0.02
11	2160	Air	1	11.8	0.00092	3.92	0.04
11	2200	Air	1-1/2	11.9	0.00058	3.97	0.03
10	2100	Air	1-1/2	11.0	0.00074	3.93	0.003

Results Using Calcining Procedure

2650	1	14.35	0.000408	3.81
2700	1	14.38	0.000421	0.04

What can be immediately seen in comparing the results is that the higher fire material has lower power factors and slightly lower dielectric constant. The bulk densities of the higher fire were slightly higher than the first fire. Polished sections made of various samples helped to explain the results.

The fire 2250°F, there was approximately 20% glass, 71% crystals and 9% pores; and in fire 2350°F there was 9% glass, 82% crystals and 9% pores. The decrease of the glass content in the second fire with the subsequent increase in the crystal content reduced considerably the amount of losses in the dielectric. This occurs since the crystal is tying up more strongly than the glass can any lossy ions which contribute greatly to the power factor. In the samples pre-fired to 2350°F there were smaller grain boundaries and an elimination of large areas of glass which occurred in the 2250°F fire. This would also tend to lower the power factor since any impurities such as mobile ions and agglomerates of unreacted material would be more evenly dispersed throughout the system thereby decreasing their effect on the losses.

It may be that the losses can be further lowered by continued heat treatment and devitrification.

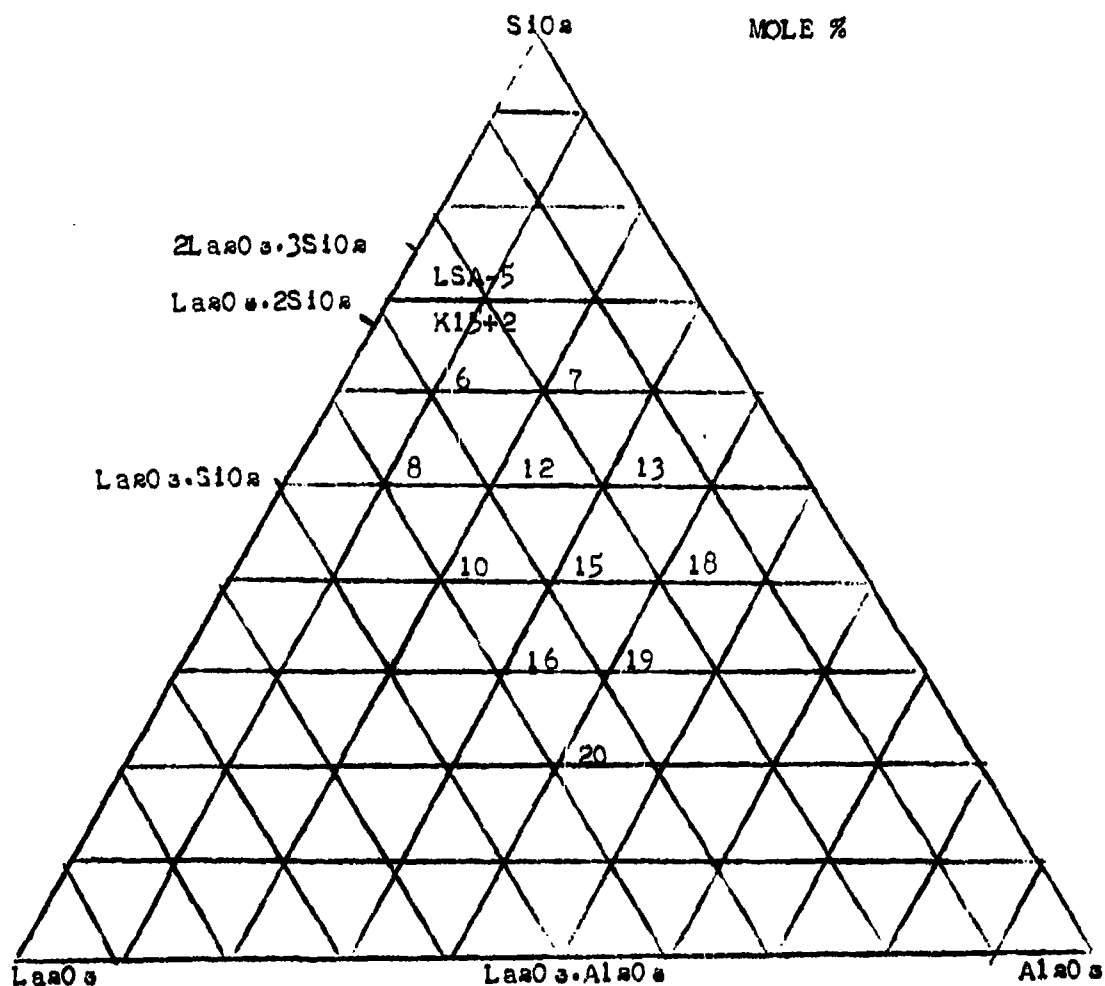
These results for the LSA-5 composition appeared to have reliability due to the results obtained by the calcining technique and due to the elimination of all but a trace amount of contamination. The fabrication technique was then utilized in the evaluation of other compositions within the ternary. The only limitations with this technique would be that the first fire could not be higher than 3400°F. The working limit of the alumina crucible, and the second fire could not exceed 3000°F, the working limit of the gas-fired kilns. Even with these limitations it was hoped that enough of the ternary system could be pre-reacted and re-fired to give information to predict the properties in the remainder of the system.

The compositions that were selected are plotted in Figure 2, and their molecular percentages are listed in Table III. Even though these compositions are in 10% increments which in most systems are too large for evaluating an entire ternary it was deemed adequate for this study.

The main reason for this is that there is no ternary composition, within the system therefore, all of the properties of the compositions will be relative to the properties of the binary compounds and their percentage within each body. The variation in this reasoning will be due to any change in the physical structure of each body such as the relation

Figure 2

MOLE %



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Table III

Molecular Percentages of Composition

	<u>LSA-5</u>	<u>K15+2</u>	<u>5</u>
La <sub>2</sub> O <sub>3</sub>	22.0	25.8	20
Al <sub>2</sub> O <sub>3</sub>	5.0	9.9	10
SiO <sub>2</sub>	73.0	64.3	70
	<u>6</u>	<u>7</u>	<u>8</u>
La <sub>2</sub> O <sub>3</sub>	30	20	40
Al <sub>2</sub> O <sub>3</sub>	60	20	10
SiO <sub>2</sub>	10	60	50
	<u>9</u>	<u>10</u>	<u>11</u>
La <sub>2</sub> O <sub>3</sub>	50	50	40
Al <sub>2</sub> O <sub>3</sub>	10	20	20
SiO <sub>2</sub>	40	30	40
	<u>12</u>	<u>13</u>	<u>14</u>
La <sub>2</sub> O <sub>3</sub>	30	20	30
Al <sub>2</sub> O <sub>3</sub>	20	30	30
SiO <sub>2</sub>	50	50	40
	<u>15</u>	<u>16</u>	<u>17</u>
La <sub>2</sub> O <sub>3</sub>	40	50	20
Al <sub>2</sub> O <sub>3</sub>	30	30	40
SiO <sub>2</sub>	30	20	40
	<u>18</u>	<u>19</u>	<u>20</u>
La <sub>2</sub> O <sub>3</sub>	30	40	50
Al <sub>2</sub> O <sub>3</sub>	40	40	40
SiO <sub>2</sub>	30	20	10

between open and closed pores; percentage of glass, crystal and pore: grain size, and crystal size. With the aid, however, of polished sections, bulk densities and moisture absorptions, most of the variations in electrical properties can be explained.

All of these compositions were prepared in the same way as composition LSA-5 and then fired in the induction furnace. With the bodies high in silica as 5, 6, 7, they became vitrified when fully reacted, and so their firing temperature could be determined by observing the slugs after firing. With bodies low in silica as 16, 19, 20, they did not become vitrified so that X-ray diffraction techniques had to be employed to determine whether or not they were properly reacted.

All of the compositions prepared except #9 and #20 were fully reacted when fired to 3400°F or below. These two compositions then had to be eliminated due to their high reacting temperature. With the second fire, all of the compositions except #10 and #16 could be matured. At 3000°F or below. Thus, both compositions #10 and #16 had to be eliminated. It must be noted here that none of the compositions had any contamination from the molybdenum except #10 and #16. Both of these compositions had slight amounts of discoloration over them when removed from the furnace. A diagram of the approximate firing temperatures is given in Figure 3.

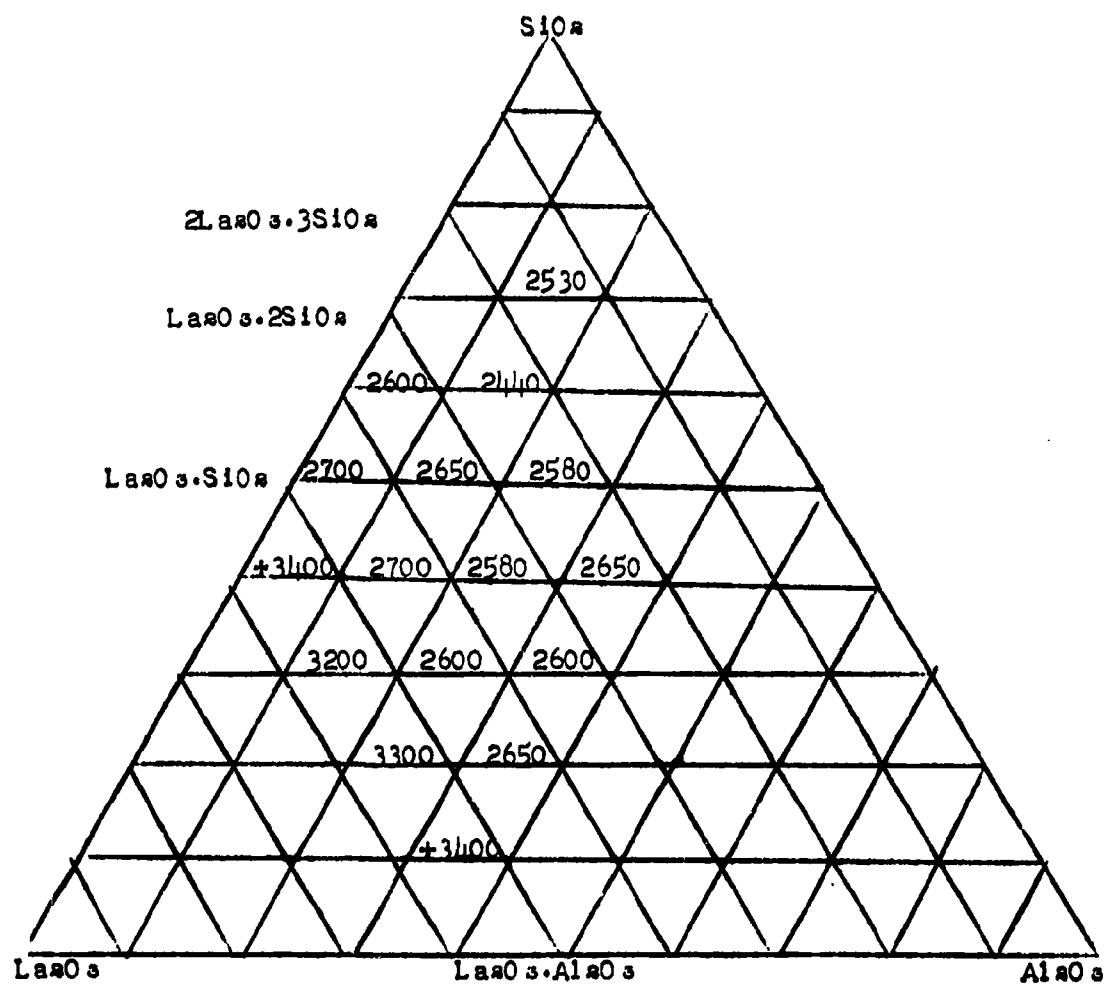


Figure 3

MOLE %

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After the compositions were crushed and passed thru a 200-mesh screen, X-ray diffraction analysis was used to determine compound formation. In none of the bodies analyzed was there any free lanthanum oxide or lanthanum hydride present. The results of the analysis are given in Table IV.

### Results

The results of this investigation are given in Table V. The dielectric constant increases as  $\text{La}_2\text{O}_3$  is maintained constant and  $\text{SiO}_2$  is replaced with  $\text{Al}_2\text{O}_3$ . This occurs because the content of lanthum aluminate is increasing and it has a dielectric content of 26. As the silica content amounts is decreased, and the  $\text{La}_2\text{O}_3$  is increased at constant alumina content the dielectric constant is increased due to the presence of  $\text{La}_2\text{SiO}_5$  which appears to have a larger dielectric constant than  $\text{Li}_2\text{SiO}_7$ .

The power factors exhibit considerable variation. The major problem here is that as was shown for the LSA-5 body. The pre-firing temperature and subsequent re-fire has a marked effect on the power factors but a minor effect on the dielectric constants. Therefore, before any absolute values can be given for these compositions further firing studies must be carried out.

Table IV

<u>X-ray Diffraction Results</u>								
<u>Compos-</u> <u>ition</u>	<u>La<sub>2</sub></u> <u>Si<sub>2</sub>O<sub>7</sub></u>	<u>La<sub>2</sub>B</u> <u>Si<sub>2</sub>O<sub>7</sub></u>	<u>La<sub>2</sub></u> <u>Si<sub>2</sub>O<sub>5</sub></u>	<u>3Al<sub>2</sub>O<sub>3</sub></u> <u>2SiO<sub>2</sub></u>	<u>LaAlO<sub>3</sub></u>	<u>Cristo-</u> <u>balite</u>	<u>Quartz</u>	<u>La<sub>2</sub>O<sub>3</sub></u>
# 5	m	M		T			T	
# 6	m	M		T				
# 7	m	m						
# 8			M	T				
#10			M		m			
#11			M	T	M			
#12	T			T	M			
#13	m	M		T				
#14	T		T	m	M			
#15			T	T	M			
#16			T		M			
#17	m	M		T				
#18	T			T	M			
#19	T			T	M			

Table V

Dielectric Properties of Compositions

At 1 Megacycle

	#5	#6	#7	#8	#9	#10	#11
K	11.0	100	9.4	13.7	---	---	14.7
D. F. (%)	.05	.47	.105	.17	---	---	.25
M Ab (%)	.01	.08	.05	.02	---	---	5.15
Bulk Density	3.83	4.25	3.57	4.89	---	---	.20
K	13.8	9.63	11.3	15.9	---	---	14.7 17.2
P. F. (%)	.73	.088	.25	.34	---	---	.6 .19
M. Ab (%)	.03	.03	.10	.11	---	---	.13 .05
Bulk Density	4.71	3.66	4.33	5.03	---	---	4.84 5.25

MgO.ZrO<sub>2</sub>.TiO<sub>2</sub> Compositions

In the quest for ceramics to fulfil the technical requirements of this problem, compositions within the system MgO-ZrO-TiO<sub>2</sub> appear promising. However, the electrical properties reported were measured at 1 mc only. The object of this phase of the work is to prepare the specimens of MgO-ZrO-TiO<sub>2</sub> compositions and to evaluate them at 8500 Mc.

The two most promising compositions in this system have the mole ratios of 2-1-2 and 4-1-4. The table below gives the compositions:

Table VI

Weight Percentage

<u>Mole Ratio</u>	<u>MgO</u>	<u>ZrO<sub>2</sub></u>	<u>TiO<sub>2</sub></u>
2-1-2	22.0	34.0	44.0
4-1-4	26.8	20.4	52.8

One hundred gram batches of each composition were weighed out. The batches were ball milled in the dry state to prevent aggregation. Discs prepared from this material were then placed on platinum foil and calcined for 4 hours at 2200°F in oxygen. The samples were then pulverized with a mullite mortar and pestle and specimens were prepared.

The second fire was also carried out in oxygen. For this fire a gas kiln was adopted to handle an oxygen atmosphere.

After firing, the discs were machined to the correct size and tolerances (1.00 + 000-.001 inches in diameter and .038 in thickness). They were cleaned and dried and submitted to the Laboratory for Insulation research at Massachusetts Institute of Technology for evaluation.

The abstract properties of these compositions measured at 1 Mc are as follows:

<u>Composition</u>	<u>K</u>	<u>P.F.</u>
2-1-2	18	.0006
4-1-4	18	.0005

Thus it is quite obvious that both compositions are effected at the high frequency. The cause is normally attributed to impurities however, the compositions as prepared for the high frequency measurements contain only the three basic oxides MgO, ZrO<sub>2</sub>, and TiO<sub>2</sub>.

The power factor as noted in the technical requirements is 0.0004 at 8500 Mc; this is extremely low. In normal insulation where the dielectric constant is in the range 5 to 10 this very low power factor is attainable only at the high frequency of interest, with single quartz crystals, single alumina crystals, very pure silica glass, and possibly with Lucalox (pure polycrystallite alumina at theoretical density). It is quite doubtful whether a body containing some glass can retain such low losses at 8.500 Mc.

Table VII

Electrical Measurements at 8.5 KMC

Composition 2-1-2

<u>Firing Temperature</u>	<u>Soak (hrs.)</u>	<u>K</u>	<u>P.F.</u>
2790	1	17.2	.0018
2790	1	19.0	.0022
2790	1	19.6	.0020
2810	1	18.1	.0016
2810	1	18.65	.0019
2810	1	17.1	.0020
2810	1	18.3	.0020

Composition 4-1-4

2800	2	17.9	.0019
2800	2	17.65	.0016
2800	2	19.65	.0021
2800	2	18.1	.0020
2800	2	17.5	.0017
2800	2	20.5	.0024
2800	2	17.9	.0020
2800	2/	17.65	.0019

Magnesium titanate possesses Dielectric Constant between 13 and 14 with a power factor at 0.001 at 1 Mc, however, it contains an appreciable impurity content. It is behind that this compound if made further pure and approaching true density that the objectives of this problem can be met.

A program has been instituted in which magnesium titanate of very high purity and fine particle size will be prepared and sintered in air. To attain optimum properties true density must be approached. If this is not attainable by firing in air the firing will be carried out in other alternate such as oxygen, hydrogen, etc.

#### Future Work

1. Compositions in the  $\text{La}_2\text{O}_3\text{-Al}_2\text{O}_3\text{-SiO}_2$  system will be further heat-treated to improve power factor.
2. Pure magnesium titanate will be prepared and evaluated at microwave frequencies.
3. Other pure refractory phases such as calcium stanates will be studied.

## Progress Report - Part IV

### HOT EXTRUSION

#### Introduction

The purpose of this work is to fabricate by hot extrusion barium titanate and other ceramic materials having the desirable properties of hot-pressed materials. Hot-pressed pieces exhibit very high densities, extremely small crystal size, high mechanical and dielectric strengths. In the case of barium titanate, hot-pressed material exhibits both a considerably higher room temperature dielectric constant and a greatly reduced rise in dielectric constant at the Curie Point than normally processed barium titanate.<sup>1</sup>

The equipment being used in this work and the procedure are described in previous reports.<sup>2</sup> The general technique that is being used employs a metal coextrusion can to serve as a lubricant for the extrusion of the ceramic. Both the ceramic and the metal can are heated to a predetermined temperature and quickly transferred to the extruder barrel for extrusion.

<sup>1</sup> A. Brown and R. Fisher, "Properties of Hot-Pressed Barium Titanate," USARL Technical Report 2196, April 1961, U. S. Army Signal Research and Development Laboratory, Ft. Monmouth, N. J.

<sup>2</sup> "Inorganic Dielectrics Research," Progress Report Nos. I, II, III. Contract No. DA-36-039-sc-89141. School of Ceramics Rutgers, The State University, New Brunswick, New Jersey

Rutgers, The State University  
Signal Corps Contract No. DA-36-039-sc-89141



The previous reports also describe the successful extrusion of a glass-mica mix in aluminum coextrusion cans.

#### Experimental Work and Discussion

A new extrusion barrel and several dies and co-extrusion cans were made during this period. These dies had extrusion ratios of only 5 to 1 and 10 to 1 since lower extrusion ratios should considerably facilitate extrusion.

The work during this period consisted of two phases. The first phase entailed attempts to produce barium titanate by slow hot-extrusion using graphite dies and no coextrusion cans. This phase was performed while waiting for the new barrel and dies to be machined.

The second phase entailed the extrusion of lead zirconate titanate in 1018 steel coextrusion cans.

#### Low Pressure Extrusion Attempts

While waiting for the machining of new parts for the hot extrusion set-up, the time was utilized in the study of whether barium titanate could be hot extruded slowly at low pressure.

For these experiments, the extrusion barrel, extrusion die, punch and push rod were all machined from CS Grade graphite.<sup>5</sup> Essentially only two types of extrusion set-ups were used, although several different extrusion ratios were tried.

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<sup>5</sup>Manufactured by the National Carbon Company

The set-up for the first extrusion attempt was of conventional type with the die located at the bottom of the extrusion barrel. The extrusion ratio was 10:1. A loose fitting graphite plug was placed in the extrusion die to keep the uncompacted barium titanate from pouring out through the die opening. This plug was left in place throughout the extrusion attempt since it was felt that the pressure of the barium titanate would push it out as extrusion occurred.

In the first extrusion attempt, the barium titanate<sup>4</sup> was packed into the extrusion barrel under a pressure of 1000 psi. No pressure was applied during heating until the temperature reached 1800°F. At this point the temperature was stabilized and a pressure of 1000 psi was applied and maintained until no further flow took place. Then the temperature and pressure were both slowly increased to 2250°F and 2800 psi respectively. At this point, the push rod broke and the run was discontinued. Although some material flow occurred, it was not enough to push the plug completely out of the die.

The same set-up was used for the second extrusion attempt except that the plug was removed from the extrusion die after the material was compacted at room temperature. This was done since it was felt that the plug may have been offering more

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<sup>4</sup> The barium titanate used in all of this work was the Titanium Alloy Manufacturing Company's Capacitor Grade.

resistance to extrusion than was original thought. A pressure of 1000 psi was applied and maintained while the temperature was raised to 2340°F. At this point the pressure was raised to 1500 psi while the temperature was held constant. When no further material movement took place, the temperature was raised to 2450°F. There was still no movement of the material so the temperature was raised to 2550°F. At this point, some material started melting and dripping out of the die opening but no overall movement of the material could be observed. The pressure was raised to 2300 psi with no observable material flow. At this point the push rod broke and the run was discontinued. Extrusion had not occurred.

A new die was made with an extrusion ratio of only 4:1 since it was felt that this would considerably facilitate extrusion. Two extrusion attempts were made with this die using temperatures as high as 2500°F and pressures up to 4000 psi, but extrusion was not accomplished.

Observations of the material flow during these experiments indicated that the material flowed very readily until it became dense. Once a high degree of densification had occurred, the material exhibited a high resistance to further movement. It was postulated that the type of extrusion set-up being used was not ideal under these conditions of flow. In this type of set-up, with the pressure being applied at the top of the

barrel and the die located at the bottom of the barrel, it was envisioned that the material compaction was progressing from the top of the barrel downward. It was felt that little if any of the pressure was being transmitted to the vicinity of the die until all of the material had been densified.

As a result of these thoughts, a new extrusion design was devised. This is shown in Figure 1. In this set-up, the die is located in the top of the barrel and is free to move through the barrel. The pressure is applied to the die itself by means of a hollow push rod. It was hoped that this design would allow extrusion of the material through the die as it was undergoing densification. Only one extrusion attempt was performed with this set-up.

The barrel was packed with barium titanate powder at room temperature and the die inserted. The temperature was raised to 1900°F with a low pressure of about 200 psi being applied to the die. At 1900°F, some material flow started to occur. The temperature was raised slowly while the 200 psi pressure was maintained. At 2100°F the pressure was increased to 1000 psi. The temperature was held constant and the pressure gradually raised slowly to 2000 psi. When the pressure held fairly constant, indicating no further movement of the material, the run was stopped. Extrusion had not occurred.

Further experiments, at higher temperatures and pressures, have not been performed to date.

#### Coextrusion in Steel Cans

Two types of 1018 steel coextrusion can were produced as shown in Figure 2. Lead zirconate titanate<sup>5</sup> was used as the ceramic material for extrusion during this work period since a number of people having experience in hot-pressing both barium titanate and lead-zirconate titanate felt that the latter exhibited better flow properties.

The ceramic powder was hand-packed into the coextrusion cans which were then painted with a solution of Phosphatherm RN.<sup>6</sup> This forms a low temperature, water soluble glass which acts as a lubricant for extrusion. This lubricant acted quite satisfactorily in all of the extrusion attempts. No galling or siezing was encountered.

The extrusion billets, consisting of the coextrusion can packed with ceramic powder were heated in an induction furnace having a graphite susceptor and graphite support for the billet. An argon atmosphere was maintained in the furnace to prevent oxidation of the graphite and the steel coextrusion can.

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<sup>5</sup> U-P-I-401, Ultrasonic Powders, Incorporated.

<sup>6</sup> Alpha-Molykote Corporation.

Some problems were encountered with temperature gradients in the billet since the top of the billet had greater radiation losses than the sides or bottom. Thus optical temperature measurements on the top surface of the billet could be considerably below the melting point while the bottom was actually melting. Also, the low thermal conductivity of the ceramic made slow heating necessary in order to more nearly equalize the temperatures of the steel can and the ceramic. Several coextrusion cans were lost due to partial melting during heating. Modification of the induction furnace design and the use of the slower heating rates have helped to overcome this problem.

The data for the experimental efforts which actually culminated in attempted extrusion will be found in Table I.

Extrusion attempt #23 did result in the coextrusion of the lead zirconate titanate inside of a steel cladding. This was only a short extrusion owing to the geometry of the set-up used. The extrusion punch did travel the full length of its stroke. However, this punch had been designed for extrusion ratios greater than the 5:1 ratio used for this run. Dies which have the same lead-in angle but different extrusion ratios will come to different heights in the extrusion barrel. The lower the extrusion ratio, the lower the die sits in the barrel. With an extrusion ratio of only

5:1, the top of the die sits quite low in the barrel and a considerable amount of the billet is not extruded by a punch that is calculated to stop before hitting in a higher extrusion ratio die.

Nevertheless, extrusion of a piece about 1" long was accomplished. The ceramic core was not concentric with the steel cladding nor was it exactly round. Although tests have not been run, the ceramic appears to be dense except for a small central portion which looks as if it was not sufficiently hot when the extrusion took place. This should be corrected by allowing a longer soak at peak temperature during the heating of the billet.

#### Summary

The coextrusion of lead zirconate titanate in a steel can was accomplished for the first time. Although this extrusion was not of the desired quality, considerable improvement in this quality is believed to be obtainable in future work.

Experiments performed in attempts to hot-extrude barium titanate at low pressure were useful in demonstrating the flow characteristics of the barium titanate. It flows very readily at low pressures (1000-2000 psi) until it becomes dense. However; once it is dense, it exhibits practically

no flow at pressures of 4000 psi, even at temperatures approaching the melting point. This leads to the rather interesting idea that one way to readily accomplish the hot extrusion of these materials may be to start with powders which are not highly compacted and achieve the compaction as the material passes through the extrusion die itself.

#### Future Work

Work will be continued on the coextrusion of lead zirconate titanate in steel cans. Extrusion ratios higher than 5 to 1 will be tried. The density and electrical properties of the extruded material will be measured. Further thought will be given to the idea of designing the system so that the compaction of the ceramic does not occur until it is passing through the extrusion die.



Table I

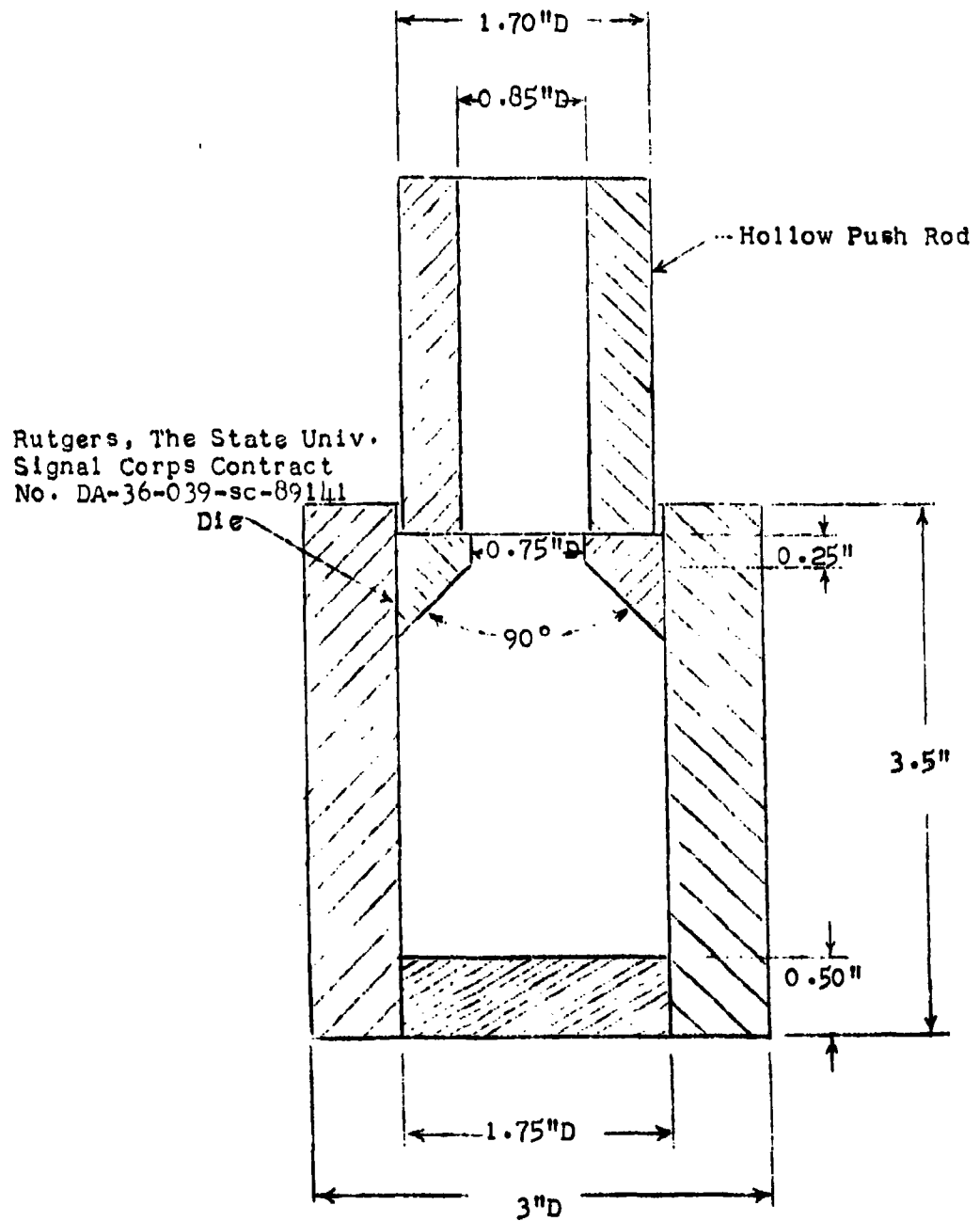
Conditions for Coextrusion Runs

Run No.	<u>Billet Materials</u>		<u>Preheating Temperature and Soak Time</u>			<u>Results</u>
	<u>Ceramic</u>	<u>Coextrusion Can</u>	<u>Billet</u>	<u>Extrusion Die &amp; Barrel</u> <sup>2</sup>	<u>Pressure psi</u>	
20	PZT <sup>1</sup>	1018 steel type 4	1800°F, 10 min.	ambient	135,000 <sup>3</sup>	no extrusion
21	PZT	1018 steel type 4	1850°F, 20 min.	ambient	135,000	no extrusion
22	PZT	1018 steel Type 3	1950°F, 30 min.	ambient	135,000	no extrusion
23	PZT	1018 steel type 4	2050°F, 30 min.	400°F	approx. 100,000	extruded

1. Lead zirconate titanate powder, U-P-1-401, Ultrasonic Powders, Inc.
2. Extrusion ratio 5:1 in all cases. Both billet and die lubricated in all cases with Phosphatherm RM, Alpha-Molykote Corporation.
3. Maximum obtainable.

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TRAVELING DIE TYPE HOT EXTRUSION SET-UP



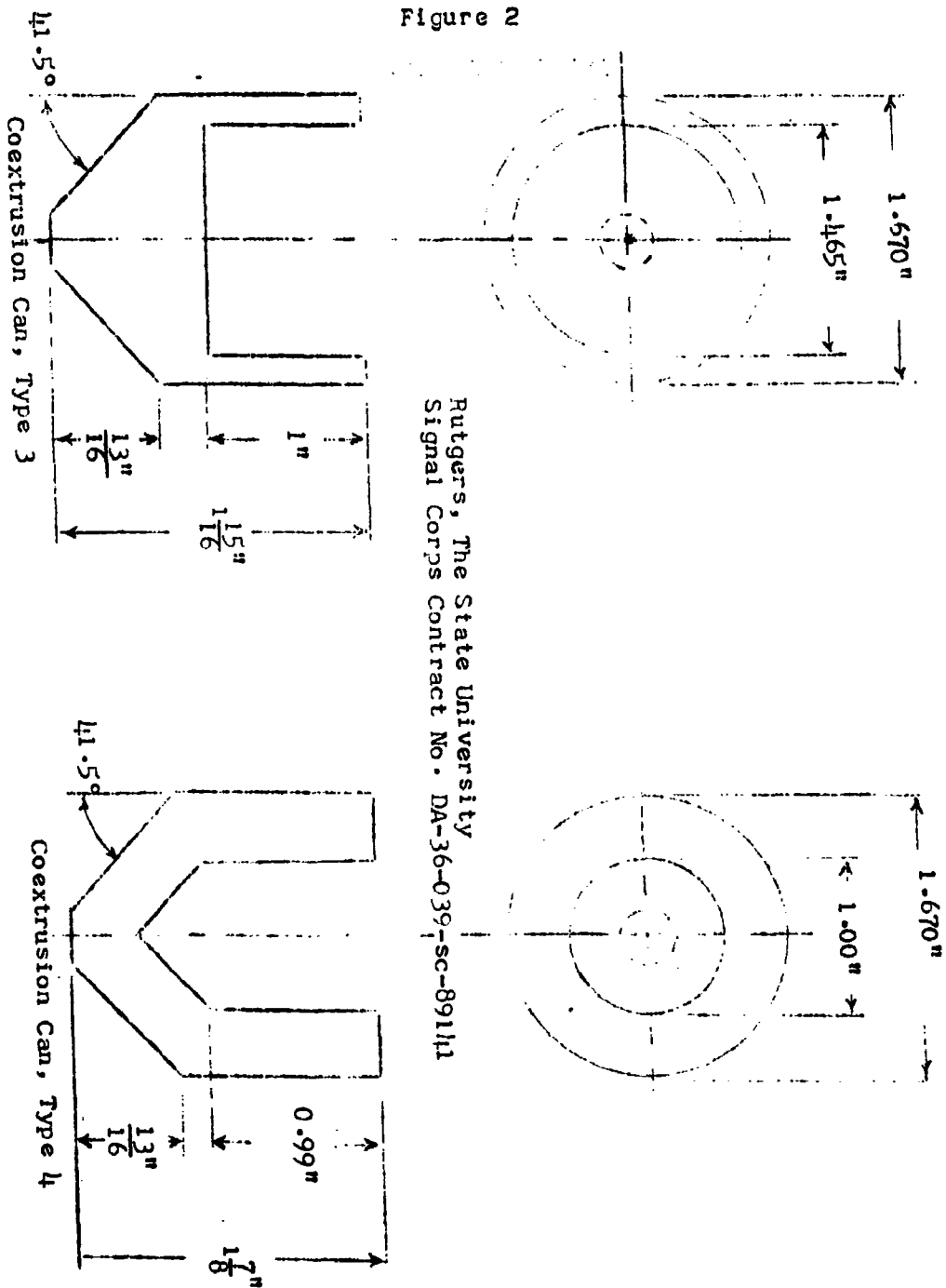
Note: All material C 5 Grade Graphite

# TWO TYPES OF 1018 STEEL COEXTRUSION CANS

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Figure 2

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<p>SCHOOL OF CERAMICS, RUTGERS, THE STATE UNIVERSITY, New Brunswick, N. J. INORGANIC DIELECTRICS RESEARCH by J. H. Koenig, E. J. Smoke, D. A. Lupfer, et al. SIGNAL CORPS REPORT NO. V, November 1, 1962 to February 1, 1963. Contract DA-36-049-SC-89141</p> <p>Unclassified report</p> <p>Under Devitrification of Barium Titanate, time-temperature studies were conducted on pressed specimen made of the ground pure barium titanate glass at several temperatures taken from the DTA curve. Petrographic studies indicate no increase in crystal size over normal firing, however, the content of crystals is increased somewhat. Dielectric constant vs. temperature and thermal expansion properties of the barium titanate glass are presented. The crystals devitrified from the barium titanate glass are more</p>	<p>UNCLASSIFIED</p> <p>( over )</p> <p>UNCLASSIFIED</p>
<p>SCHOOL OF CERAMICS, RUTGERS, THE STATE UNIVERSITY, New Brunswick, N. J. INORGANIC DIELECTRICS RESEARCH by J. H. Koenig, E. J. Smoke, D. A. Lupfer, et al. SIGNAL CORPS REPORT NO. V, November 1, 1962 to February 1, 1963. Contract DA-36-049-SC-89141</p> <p>Unclassified report</p> <p>Under Devitrification of Barium Titanate, time-temperature studies were conducted on pressed specimen made of the ground pure barium titanate glass at several temperatures taken from the DTA curve. Petrographic studies indicate no increase in crystal size over normal firing, however, the content of crystals is increased somewhat. Dielectric constant vs. temperature and thermal expansion properties of the barium titanate glass are presented. The crystals devitrified from the barium titanate glass are more</p>	<p>UNCLASSIFIED</p> <p>( over )</p> <p>UNCLASSIFIED</p>

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